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Review

Performance analysis of polymer electrolyte membranes for direct methanol fuel cells



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HIGHLIGHTS

- This review discusses recent advances in polymer electrolyte membranes for DMFCs.
- The PFSA and SAP membranes show remarkable performances at temperatures up to 90 °C.
- The composite membranes appear more suitable for DMFC applications above 100 °C.

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ABSTRACT

The status of research and development of polymer electrolyte membranes (PEMs) for direct methanol fuel cells (DMFCs) is described. Perfluorosulfonic acid membranes, e.g. Nafion, are widely used in fuel cell technology; but, despite their success, they show some drawbacks such as high cost, limited operating temperature range and high methanol crossover. These limit their widespread commercial application in DMFCs. Such disadvantages are inspiring worldwide research activities for developing new PEM materials based on non-perfluorinated polymers as alternative to Nafion for DMFCs. A review of membrane properties is carried out on the basis of thermal stability, methanol crossover and proton conductivity. The analysis of DMFC performance covers perfluorosulfonic acid membranes (PFSA), sulfonated aromatic polymers (SAPs) and composite membranes. PFSA membranes are suitable materials in terms of power density, SAPs are more advantageous regarding the low methanol permeability and cost, whereas composite membranes are more appropriate for operation above 100 °C. DMFC power density values reported in literature show that, although there are remarkable research efforts on this subject, the achieved results are not yet satisfying. Further work is especially necessary on non-perfluorinated polymers to improve performance and durability for an effective application in practical DMFC devices.

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1. Introduction

Low temperature fuel cells are emerging technologies for the electrochemical conversion of the chemical energy of a fuel directly into electric energy with low environmental impact and high-energy efficiency. Nevertheless, before this technology can reach very large scale diffusion, some problems related to poor electrochemical performance, high cost of fuel cell systems, long term stability, etc. must be solved. In a fuel cell system, high costs derive from the use of noble metal catalysts, perfluorosulfonate polymer electrolyte membranes, bipolar plates and auxiliary components. Up to now, Nafion-type polymer electrolyte membranes (Nafion is a perfluorosulfonic acid polymer produced by DuPont) are the most

widely used polymer electrolytes in H₂/air and direct methanol fuel cells. This wide use is due to the high proton conductivity, excellent mechanical and thermal properties, and high chemical and electrochemical stability of Nafion. Other similar perfluorinated polymers commercialized by Dow Chemicals (XUS®), Asahi Kasei (Aciplex-S®), Solvay (Aquivion®), Fumatech (Fumion®), Asahi Glass Engineering (FlemionR®) are under consideration worldwide. However, although perfluorinated membranes show excellent properties, they have also some disadvantages such as high cost, high methanol crossover, fast dehydration with a decrease of proton conductivity as the temperature increases above 100 °C, and loss of fluorine species in the exhaust gas due to ·OH radicals attack. Because of these constraints, there is a strong interest in the R&D of new and cheaper membranes with similar or higher conductivity and lower fuel cross-over for application in the range of temperature from 100 to 150 °C. Most of the new types of PEMs under investigation for DMFC or PEMFC applications are currently

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synthesized by using various approaches, such as the synthesis of new ionic random and block copolymers, graft copolymerization of ionic polymers on hydrophobic membranes, blending of ionic and non-ionic polymers, synthesis of interpenetrating networks of ionic and non-ionic polymers and composite membranes incorporating a large variety of fillers (silica, zeolites, titania, zirconia, etc.).

2. Recent literature regarding polymer electrolytes for fuel cell applications

In the years from 1994 to 2012, wide research activities toward the development of new polymer electrolytes for DMFC applications were carried out as demonstrated by the trend of publications per year in Fig. 1 (the number of publications for the year 2013 is essentially limited to the first four months), and great efforts and progress were made in this topic of research. The number of papers concerning with this subject was performed by searching into Scopus database (www.scopus.com; Scopus® is a registered trademark of Elsevier BV Netherlands) by using a combination of different keywords to identify the current literature in the field of polymer electrolytes and membranes for direct methanol fuel cells. The following keywords were used in TITLE-ABS-KEY ("Fuel cell" OR "Fuel cells") AND (LIMIT-TO (EXACTKEYWORD, "Methanol") OR LIMIT-TO (EXACTKEYWORD, "Direct methanol fuel cells (DMFC)") OR LIMIT-TO (EXACTKEYWORD, "Direct methanol fuel cell") OR LIMIT-TO (EXACTKEYWORD, "Ethanol") OR LIMIT-TO (EXACTKEYWORD, "DMFC") OR LIMIT-TO (EXACTKEYWORD, "DMFCs")). The keywords used in this search do not allow a complete separation of the papers with a subject regarding the polymer electrolytes and those relative to other types of studies, e.g. catalysts, electrodes, modeling, etc. for DMFCs. The search was performed on 10 May 2013.

With the data extracted from Scopus, a "DMFC membranes" database was created from which a list of published papers per year was generated.

A total of 6890 publications were selected for the analysis, of which 5792 are papers from journals, 887 are publications from conference proceedings (including ECS Transactions), 113 are book series and 98 are trade publications. From Fig. 1, it is evident that there is a gradual increase in publications per year in the range from 1994 to 2000, and that in 2001, 2004 and 2008 there are apparent strong jumps. In 2001, 109 papers have been published with respect to 52 of 2000, in 2004, 416 papers with respect to 231 of 2003, in 2008 710 against 589 of 2007. The peak of productivity has been reached in 2010 with 834 while in 2011 and 2012 the number of

papers slightly decreased to 746 and 701, respectively. A detailed analysis of the scientific contents of the publications shows that there is a strong interest in the subject "polymer electrolytes" for DMFCs.

2.1. Highlighting the research in polymer electrolytes for direct methanol fuel cells

In the following sub-paragraphs the most important findings of recent investigations on polymer electrolytes for DMFCs are discussed.

2.1.1. Perfluorosulfonic acid membranes

Perfluorosulfonic polymers, naturally combine in one macromolecule, the very high hydrophobicity of the perfluorinated backbone with the extremely high hydrophilicity of the sulfonic acid functional groups. These polymers, in the presence of water, give rise to some hydrophobic/hydrophilic nano-separation. The sulfonic acid functional groups aggregate to form large hydrophilic domains. When these are hydrated, proton conductivity assisted by water occurs. While the well connected hydrophilic domains are responsible for the transport of protons and water, the hydrophobic domain provides the polymer with an adequate chemical and mechanical stability and avoids that the polymer is dissolved in water [1]. The main advantages of perfluorosulfonic acid (PFSA) membranes are: (i) their strong stability in oxidative and reduction media due to the structure of the polytetrafluoroethylene backbone; and (ii) their proton conductivity, which can be as high as 0.2 S cm^{-1} in polymer electrolyte fuel cells (PEFCs) [2]. Yet, when used at elevated temperatures, PEFC performance decreases due to (i) dehydration of the membrane, (ii) reduction of ionic conductivity, (iii) decrease in affinity with water, (iv) loss of mechanical strength through a softening of the polymer backbone, and (v) parasitic losses (because of a high level of gas permeation). Perfluorosulfonic membranes (Nafion, Flemion, Aciplex, Aquivion, Fumion, etc.) are currently used as electrolytes in DMFCs [3]; yet, since methanol is rapidly transported across these membranes and is chemically oxidized to CO_2 and H_2O at the cathode, there is a significant decrease in coulombic efficiency for methanol consumption by as much as 20% under practical operation conditions. Thus, it is very important to modify these membranes by, for example, developing composites [4–7] or synthesizing alternative proton conductors with the capability of inhibiting methanol transport. The polymer electrolyte should have a high ionic conductivity under working conditions and a low permeability to methanol (less than $10^{-6} \text{ mol min}^{-1} \text{ cm}^{-2}$). Furthermore, it must be chemically and electrochemically stable under operating conditions. Potentially, these requirements appear to be met by new classes of solid polymer electrolytes that show promising properties for applications in DMFCs. A review of these new types of polymers is reported in the following paragraphs.

2.1.2. Poly(styrene)-based electrolytes

A number of sulfonic-acid containing random copolymers was investigated for DMFC applications. Sulfonated poly(styrene) (SPS) [8–11], random copolymers of poly(styrene) and poly(styrene sulfonic acid) (PSSA) [11–13] were the most investigated poly(styrene)-based materials in DMFCs. Additionally, sulfonated crosslinked polystyrene was also used with poly(vinylidene fluoride hexafluoropropylene) copolymer/Nafion® blend [14] and chemically crosslinked poly(vinyl alcohol)/poly(2-acrylamido-2-methyl-1-propanesulfonic acid)/poly(vinylpyrrolidone) blend [15]. SPS can be synthesized either by copolymerizing styrene and styrene sulfonic acid monomers or by post-sulfonation of poly(styrene) with different sulfonating agents (e.g., acetyl sulfate,

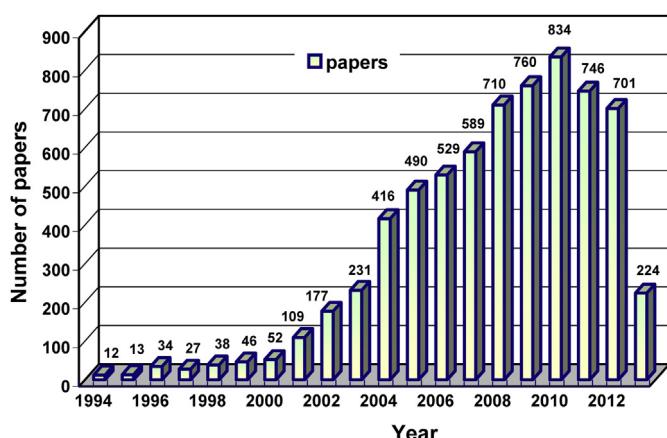


Fig. 1. Summary of the number of papers published per year extracted from Scopus database regarding the polymer electrolyte membranes for direct methanol fuel cells.

sulfur trioxide). The post-sulfonation method of commercial available polymers consists of an electrophilic substitution reaction of sulfonic acid in the aromatic group of the polymer backbone, which is a common method used to synthesize sulfonated polymers from entirely aromatic-based polymers. These reactions are widely used to modify the characteristics of random copolymers, in which the ion exchange capacity or sulfonic acid content in the polymer can be controlled by reaction conditions.

A more detailed discussion about synthesis, thermal and chemical properties and electrochemical characteristics of these polymers and membranes can be found in specific reviews [16,17].

2.1.3. Other non-perfluorinated polymer electrolytes

Aromatic polymers are considered to be one of the most promising routes to obtain high performance polymer electrolytes because of their ready availability, processability, wide variety of chemical composition and potential stability in the fuel cell environments. Specifically, poly(arylene ether) type-polymers such as poly(arylene ether ether ketone)s (PEEKs), poly(arylene ether sulfone)s, polysulfones, poly(imide)s, polybenzimidazoles and their derivatives are currently under investigation. The synthesis of these polymer materials is in development as shown from the increasing number of publications per year (Fig. 1) especially in this last decade. These families of polymers are very attractive for use in PEMs because of their well-known oxidative and hydrolytic stability under harsh conditions.

Introduction of ion exchange groups to poly(arylene ether)s has been accomplished by both a polymer post-modification approach and a direct co-polymerization of sulfonated monomers.

The post-modification method used to modify aromatic polymers for DMFC and PEMFC applications occurs by electrophilic aromatic sulfonation. Aromatic polymers are easily sulfonated using concentrated sulfuric acid, fuming sulfuric acid, chlorosulfonic acid, or sulfur trioxide. However, with the post-modification method, a large variation of properties of the final polymer is obtained because of the lack of a precise control on the functionalization degree and location of functional groups, the possibility of side reactions, or degradation of the polymer backbone. Yet, nowadays they offer the advantage of using commercial available high performance polymers.

Poly(ether ether ketone)s (PEEKs) and poly(ether ether ketone)s (PEEKKs) [10,18–20] are semicrystalline and highly stable polymers with extremely good thermal and chemical stability that can be sulfonated through either polymerization or post-sulfonation techniques producing random copolymers with sulfonic acid substituted directly to the aromatic backbone. The sulfonated poly(ether ether ketone) (SPEEK) [20] is generally amorphous because sulfonic groups introduce modifications in the symmetry of polymer structure. These polymers show interesting properties for DMFCs such as low methanol cross-over, good hydrolytic and thermal stability, high mechanical strength, and satisfactory ion conductivity.

Liu et al. [20] synthesized SPEEK membranes directly from the sulfonated monomer and proposed their possible application in fuel cells. They found that the direct synthesis of the SPEEK from sulfonated monomer was more advantageous than the post-sulfonation method. Li et al. [21] prepared SPEEK membranes with various degrees of sulfonation (DS). The proton conductivity as well as methanol permeability of the SPEEK membranes was found to increase as the DS increased. Due to the different microstructure, the methanol permeability of SPEEK membranes was about one order of magnitude lower than that of Nafion® 115 membrane over the temperature range from 25 to 80 °C.

The development of polymer electrolytes based on poly(ether ether ketone)s is under current study because of their excellent

characteristics. Recent excellent reviews reported complete information and details on properties and features of these membrane materials [16,22–24].

Poly(aryl ether sulfone)s are aromatic polymers commercialized for more than three decades. They show unique combination of good chemical and physical properties, including high stability to hydrolysis, high thermal stability and good transparency, when they are in the amorphous phase.

Polysulfones (PSUs) and poly(ether sulfone)s (PESs) have been widely used as membrane materials for gas separation, ultrafiltration, pervaporation and electrodialysis because of their high chemical and thermal stability, high glass transition temperature (T_g) as well as their good film-forming properties and solubility in aprotic solvents, such as 1-methyl2-pyrrolidone (NMP) and *N,N*-dimethylacetamide (DMAc). A large number of commercial polysulfones was prepared by variation of bisphenol moieties. Sulfonation of poly(arylene ether sulfone)s can be obtained by two different routes. The most suitable and often applied way to obtain functionalised, and in particular sulfonated, polymers is the post-treatment of the base polymer. The other way is the copolymerization, starting from sulfonated monomers. The post-sulfonation method consists in an electrophilic substitution on the aromatic ring. Depending on the chemical composition of the polymer backbone and the final degree of sulfonation, various sulfonating agents with different reactivity can be selected and used on commercially available poly(arylene ether sulfone) materials. Although post-sulfonation of poly(arylene ether sulfone)s is an easy and high-yield process, it can have some disadvantages as degradation of polymer backbone and non-homogeneity during phase reaction. Various authors [25–27] studied the synthesis conditions of different poly(arylene ether sulfone)s and their influence on the physical–chemical and electrochemical properties of the membrane.

These sulfonated aromatic PEMs prepared by post-sulfonation of commercial polymers are characterized by random distribution of hydrophilic and hydrophobic domains. To understand how the PEM morphology influences the phase separation between hydrophilic and hydrophobic domains as well as the connectivity between hydrophilic domains also at low relative humidity (RH), different strategies for the synthesis have been attempted in order to improve the electrochemical properties of sulfonated aromatic PEMs. These include the synthesis of multiblock or grafted copolymers with controlled segment length. Yang et al. [28,29] reported on the preparation of polysulfone-block-PVDF copolymers. The sulfonation of the polysulfone was conducted with trimethylsilyl chlorosulfonate and the degree of sulfonation was controlled by the amount of sulfonating agent added to the reaction mixture. As a result, the block copolymers showed higher proton conductivities at ion exchange capacities (IECs) < 1.4 mmol g⁻¹ than sulfonated homopolymers with comparable IECs. For polymers with low IEC (ca. 0.8 mmol g⁻¹), the conductivity improved by a factor of 4 over a temperature range from 30 to 80 °C.

The McGrath's group extensively studied the use of sulfonated 4,4'-dichloro diphenyl sulfone in combination with various bisphenols, such as bisphenol A, bisphenol 6F, hydroquinone for the preparation of multi-block copolymer materials. Their main results were published in a dedicated review [30]. High proton conductivities were obtained with a copolymer containing bisphenol moieties. For example a polymer with 40 mol% of the sulfonated monomer (IEC = 1.7 mmol g⁻¹) showed a proton conductivity of 0.1 S cm⁻¹ at 25 °C, whereas a polymer with 30% sulfonated monomer (IEC = 1.3 mmol g⁻¹) had a conductivity of 0.04 S cm⁻¹. The value of proton conductivity for Nafion® 1135 studied under same condition (IEC = 0.91 mmol g⁻¹) was 0.11 S cm⁻¹. Phase separated morphologies were reported and hydrophilic domains

were ranging from 10 to 25 nm, depending on the degree of sulfonation. At sulfonation levels higher than 50% (50 mol% of sulfonated monomer), a phase inversion was observed using atomic force microscopy. These findings correlated very well with the increase of water uptake of this polymer. Such poly(arylene ether sulfone) membranes showed similar or even better performance in both hydrogen/air and especially direct methanol fuel cells than Nafion® 117 membranes [30]. The long-term tests in a hydrogen/air fuel cell (800 h at 80 °C, 0.5 V, and 100% R.H.) revealed a high stability of the poly(arylene ether sulfone) under these conditions. In DMFC tests, for example, a membrane of poly(arylene ether sulfone) of IEC = 1.35 mmol g⁻¹ (35 mol% of sulfonated monomer) gave a current density of 210 mA cm⁻² at 0.5 V, while the Nafion 117 gave 180 mA cm⁻². In a further study, the same group [31] reported that disulfonated poly(arylene ether benzonitrile) copolymers of hexafluoro-isopropylidene diphenol (6F), 2,6-dichlorobenzonitrile with an IEC of 1.32 mmol g⁻¹ showed a 33% higher current density at 0.5 V than that of the above discussed poly(arylene ether sulfone) membranes (IEC 1.70 mmol g⁻¹) and recast Nafion® 1100 membrane with comparable thickness. A range of proton conductivities between 0.01 and 0.1 S cm⁻¹ was found for many families of polymer membranes as discussed in the paper [32]. The membranes with fluorinated groups showed a slightly higher water uptake and approximately exhibited 2-fold lower methanol permeability than Nafion. These findings demonstrated that the performance loss of ion-exchange membranes at elevated temperatures might not only be due to dehydration but also depends on morphological changes as indicated by the comparison of the ion conductivities measured at elevated temperatures.

Poly(imide)s have received considerable interest because of their excellent thermal and chemical stability [33–40]. Specifically, six-member rings of poly(imide)s are favored compared to five-member rings of poly(imide)s because of their lower ring strain and better hydrolytic stability. McGrath and coworkers polymerized disulfonated polyimide random copolymers obtaining degrees of sulfonation as high as 86 mol% (two sulfonic acid groups per monomeric unit) [41–43]. Proton conductivity and methanol permeability of 12 mS cm⁻¹ and 8.00 × 10⁻⁷ cm² s⁻¹, respectively, were reported. Another study reported the synthesis of polyimide containing trifluoromethyl groups. The membrane showed a 70% lower methanol crossover compared to Nafion® [44]. However, should be considered that in direct methanol fuel cells, the methanol/water solution chemically interacted with the PEM backbone as in polyimide membrane causing plasticization phenomena, which modified the MeOH permeability characteristics.

Other families of interesting polymers are the poly(phosphazene)s, which are inorganic polymers with a backbone consisting of alternating phosphorus and nitrogen atoms, with two side groups attached to each phosphorus. These polymers can be synthesized with various structures by changing side chain groups that are able to improve their thermal and chemical stability in different operating conditions [45]. These side groups can be aliphatic, aromatic, inorganic or also organometallic compounds. The sulfonation of these polymers can be obtained by post-sulfonation reaction, which is generally easy to carry out, whereas the direct synthesis can be preferred with functionalized polyphosphazenes due to the better control of properties and the minimization of side reactions, including reactions of degradation of the polymer structure.

Allcock's group [46] synthesized sulfonated and crosslinked poly[(aryloxy)phosphazene] by using gamma radiation and obtained proton conductivity values approximately half of those of Nafion. Moreover, these membranes exhibited at room temperature permeabilities about 40 times lower than Nafion 117 membrane. Guo et al. [45] and Tang et al. [47] found that sulfonated poly[bis(3-methylphenoxy)phosphazene] offered a combination of

good proton conductivity, cross-linkability and low methanol permeability; features which are especially important for direct methanol fuel-cell membranes. UV-crosslinked membranes prepared from SPB3MPP of IEC 1.4 mmol g⁻¹ exhibited a methanol diffusion coefficient on the order of 1.0 × 10⁻⁷ cm² s⁻¹, which was significantly smaller than that obtained with Nafion 117 in a temperature range from 20 to 70 °C. These membranes exhibit good thermo-mechanical strength up to 170 °C. The Pintauro's group [48] prepared blends of sulfonated poly[bis(phenoxy)phosphazene] (SPOP) and polybenzimidazole (PBI). The study showed that increasing PBI content resulted in a decrease of conductivity. This was attributed to increased reactions of cross-linking, which resulted in reduced water sorption and the immobilization of protons by interaction with the basic sites of PBI, limiting charge transport. Overall, selectivity (i.e. ratio proton conductivity/methanol permeability) of SBPOP-PBI membranes was approximately twice than that of Nafion® with methanol permeability ranging from 1.2 × 10⁻⁶ to 1.2 × 10⁻⁷ cm² s⁻¹, which was from 3 to 20 times lower than Nafion®. Slightly lower DMFC performance compared to Nafion® was reported. Moreover, problems of contact resistance due to a delamination between the SBPOP-PBI membrane and the Nafion® binder in the catalyst layer of electrodes were observed.

An extended overview of research and development on poly-phosphazene polymer materials of interest in the field of polymer electrolyte membranes for fuel cells was reported in recent reviews [49,50].

Other families of alternative membranes are the acid-doped polybenzimidazoles (PBIs). In a more wide definition of PBI polymers, we also refer to a large family of aromatic heterocyclic polymers containing benzimidazole units. PBI with different structures can be synthesized from hundreds of combinations of tetra-amines and diacids [51]. More in general PBI is intended the commercial product under the trademark Celazole®, poly-2,2'-*m*-(phenylene)-5,5'-bibenzimidazole. In the PBI context of different possible polymer structures this specific PBI is also named as *m*PBI because the phenylene ring is meta-coordinated. The PBI based membranes are usually prepared by casting from solutions of high molecular weight PBI in dimethylacetamide (DMAc). The subsequent membranes were made proton conductive by immersion into solutions of phosphoric acid (generally 11 M). PBI is a basic polymer (*pKa* = 5.5), upon doping with acid, it forms a single-phase polymer electrolyte that has a good oxidative and thermal stability, and mechanical flexibility at elevated temperatures (100 °C < *T* < 200 °C) together with high proton conductivity, low electro-osmotic drag and slight lower cost than Nafion membranes [3,52]. The main question that is arising for the practical use of acid doped PBI membranes concerns with the leaching of acid (H₃PO₄) trapped in the polymer, during operation of a fuel cell fed with a hot methanol/water mixture as the anode reactant. In fact, these membranes usually swell at high temperature in the presence of water and methanol. These problems could be probably better addressed by using a high molecular weight super-acid such as phosphotungstic acid [53] that may be physically entrapped in the polymer structure.

A similar approach, in which the proton conductivity is not so critically dependent on the ionic groups concentration and water content, as in the perfluorinated membranes, and the methanol crossover is controlled or, ideally, prevented, is based on the development of nano-porous proton conducting membranes (NP-PCM) [54,55]. These membranes consists of (i) high-surface-area inorganic, electronically nonconductive powder consisting of nanosize (15 nm or less) particles with good retention capability for aqueous acids (suitable materials are, among others, silica, zirconia, titania, or alumina); (ii) polymer binders like polyvinylidene fluoride (PVDF); (iii) aqueous acid or mixtures of acids which fill the

nano pores. Also, for these types of membranes, the leakage of acids during the normal operation in fuel cells with methanol fuel is an issue that must be carefully considered.

2.1.4. Polymer electrolytes based on grafted copolymers

Several papers reported on grafted SPS or PSSA on a variety of hydrophobic polymers, such as poly(ethylene-tetrafluoroethylene) (ETFE), poly(vinylidene fluoride) (PVDF), and low-density poly(-ethylene) (LDPE). In these studies, a grafting process was carried out by exposing the hydrophobic polymer membrane to a radiation source, which promotes the formation of radicals and functional groups on the membrane. This was followed by grafting and copolymerization of styrene or styrene sulfonic acid monomers.

A recent study investigated two commercial grafted copolymer membranes: an IonClad® R-1010 membrane, composed of PSSA side chains grafted to a perfluorinated polymeric backbone, and an IonClad® R-4010 membrane, composed of PSSA grafted to a tetrafluoroethylene/perfluoropropylene copolymer [56]. Proton conductivities were similar to Nafion, while methanol permeabilities were four times lower. Scott et al. [57] studied the behavior of radiation-grafted SPS with low-density polyethylene and ETFE and compared their electrochemical features in fuel cells with those obtained with Nafion® 117. They found for these membranes comparable or even better DMFC performance at higher current densities than Nafion, but however delamination phenomena at the interface between catalyst layer and membrane was an important drawback that should be solved for the MEA durability.

Hatanaka et al. [58] investigated the relationship between the degree of grafting and proton conductivity for membranes consisting of PSSA grafted on ETFE. Methanol and water uptakes increased linearly with the degree of grafting, and the selectivity for water to methanol was higher compared to Nafion. Methanol permeability experiments showed a 30% decrease compared to Nafion®, however, the fuel cell performance of these grafted copolymer membranes was lower than Nafion.

Gubler et al. [59] reported a study on radiation grafting membranes of styrene/divinylbenzene onto poly(ethylene-alt-tetrafluoroethylene) with an optimum grafting level varying between 20% and 30%. In this range of grafting, the fuel cell performance was comparable to Nafion, and a durability test over 770 h did not show any membrane degradation.

More details on syntheses, properties and features of radiation-grafted membranes can be found on specific reviews [60,61].

2.1.5. Polymer electrolytes based on block copolymers

A number of sulfonic acid containing block copolymers has been synthesized for DMFCs. Block copolymers are chemically attractive because they hold both ionic and non-ionic monomers on the same polymer backbone in an ordered sequence. Block copolymers provide a unique template, where microphase separation occurs on a nanometer scale due to the thermodynamic instability between different blocks forming a variety of morphologies. Early studies on sulfonated block copolymers were addressed only to the sulfonation and to the structural and thermal characterization of styrene-based block copolymers with low ion exchange capacities (IECs). Recently, a number of investigators has examined the ion transport properties of sulfonated block copolymers and has found conductivities comparable to Nafion. Various research groups have examined sulfonated poly(styrene-b-ethylene-r-butylene-b-styrene) (S-SEBS) [62,63]. The styrene block of SEBS was sulfonated with a standard post-sulfonation method. Similarly to sulfonated polystyrene polymers, S-SEBS showed that both proton conductivity and methanol permeability increased with the increasing of sulfonation level. For these membranes, proton conductivities and selectivities (ratio between

conductivity and methanol cross-over) similar to those of Nafion were reported.

Elabd et al. [64] studied a triblock copolymer of sulfonated poly(styrene-isobutylene-styrene) (S-SIBS), at various sulfonic group contents. Methanol permeabilities in S-SIBS were more than an order of magnitude lower than Nafion 117, and conductivities were only three-fold less at ambient conditions. S-SIBS was approximately 5–10 times more selective than Nafion 117 over an ion content range from 0.5 to 1.0 mmol g⁻¹.

Okada's group [65] investigated proton-conducting membranes based on chemically cross-linked PVA-PAMPS [poly(vinyl alcohol) and poly(2-acrylamido-2-methyl-1-propanesulfonic acid)] composites. They showed an application of the well established concept of PVA-PAMPS semi-interpenetrating polymer network (semi-IPNs) by incorporating poly(ethylene glycol) bis(carboxymethyl) ether (PEGCME) as a plasticizer. The polymer was based on a relatively low content of PAMPS as a component of ion conducting sites, the resulting semi-IPN exhibited high proton conductivity 0.1 S cm⁻¹ at 25 °C and a power density of 51 mW cm⁻² at 80 °C. Another interesting feature of this material is that a good performance is achieved for 130 h of stable DMFC operation. The good DMFC performance was believed due to suppression of methanol crossover.

Walker et al. [66] developed interpenetrating network (IPN) membranes of crosslinked P(AMPS-co-HEMA) and PVA. Free-radical copolymerization and crosslinking of AMPS and HEMA were performed in a PVA matrix. PVA was crosslinked in a successive step with glutaraldehyde. These IPNs were thermally stable up to 150 °C, and further investigations were conducted using these membranes in DMFCs over 100 °C.

Yamaguchi's group [67] developed polymer-filled microporous membranes in comparison to cross-linked polymers by using both experimental and theoretical tools. Their results demonstrate that polymer-filled microporous membranes can effectively suppress the same amount of swelling as highly crosslinked polymers, while increasing selectivity. A recent study [68] showed results on DMFC application, in which the polymer-filled microporous membranes demonstrated an increased proton conductivity without a significant increase of methanol crossover.

Since the desired material properties cannot always be found in a single polymer or copolymer material, the polymer blending and/or composite/hybrid formation processes are current strategies to improve and to adjust the physical and electrochemical properties of polymer membranes.

2.1.6. Composite polymer membranes

Considerable efforts have been addressed in the last decades to the development of composite membranes for DMFCs. These include ionomeric membranes modified by dispersing inside their polymeric matrix insoluble acids, oxides, zirconium phosphate and coating the surface with barrier polymer or deposition of sulfonated polyvinyl alcohol (PVA) [2–4,69–72]. Other examples are ionomers or inorganic solid acids with high proton conductivity, embedded in porous nonproton conducting polymers [7]. In situ formation of the filler inside the membrane can also be accomplished by using a sol–gel type procedure e.g. in the case of silica by using tetraethyl orthosilicate (TEOS) as precursor [73].

The composite membrane approach was used in DMFCs to increase the operating temperature (up to 145 °C) and reduce methanol cross-over by effect of an increase in the tortuosity factor in the permeation path for methanol permeation. Nanoceramic fillers have been included in the polymer electrolyte network to accomplish not only these two effects but also to improve membrane stability in concentrated methanol solutions both in terms of hydrolytic and mechanical aspects.

Although it has been hypothesized [73,74] that the inorganic filler induces structural changes in the polymer matrix, the water retention mechanism and the protonic conductivity appear more likely to be favored by the presence of acidic functional groups on the surface of nanoparticle fillers [75]. Composite recast Nafion-silica membranes have shown excellent properties in terms of mechanical characteristics, water retention at high temperature, resilience to methanol cross-over and ionic conductivity [69]. These electrolytes can suitable operate at both ambient temperature and high temperature (up to 145 °C) with a significant enhancement in methanol oxidation kinetics [69].

Significant improvements have been also obtained with silica-modified sulfonated polysulfone [76] and similar hydrocarbon membranes such as S-PEEK [77].

In general, the addition of inorganic fillers allows to achieve both an increase of conductivity at temperatures higher than those allowed by unfilled polymer membranes and a reduction of methanol permeability. Whereas the main effect of membrane modification by PVA regards the reduction of the cross-over during fuel cell operation [78,79]. The improvements induced by the modifications above discussed are effective for almost all polymer electrolyte families e.g. perfluorosulfonic, polystyrene-based, poly(arylene ether ketone)s, poly(benzimidazole)s, poly(arylenesulfone)s, poly(vinyl alcohol) and other polyarylene-based membranes [78,79].

Regarding the mechanism of conductivity improvement at high temperature, in the presence of humidification constraints, it has been observed that an increase in both strength and amount of acidic surface functional groups on the fillers surface is effective in enhancing the water retention inside the composite membranes through an electrostatic interaction, as it occurs for the adsorption of hydroxyl ions in solution [72,75]. Thus, as above-mentioned, the water retention in composite membranes is promoted by the presence of acidic functionalities on the filler surface. This approach has allowed DMFC operation at high temperature (145 °C) and

reasonable pressure (1.5 bar, abs) with acceptable level of performance [6,75].

2.2. Proton conductivity and methanol permeability of polymer electrolyte membranes

As well-known the proton conductivity and methanol permeability of polymeric membranes generally increase with increasing of the ionic groups concentration and temperature. In particular, an increased ionic groups concentration leads to a higher water uptake and thus higher conductivity; on the other hand it produces an increase of the methanol cross-over. However, it is also experimentally demonstrated that a high water content in the membranes produce a loss of mechanical strength and worsening of water management in single cells or in stacks. Also, when temperature increases (>100 °C) the membranes dehydrates producing a reduction of proton conductivity and water content. Accordingly, for polymer electrolytes based on sulfonic acid groups, proton and methanol transport usually follow the same behavior, e.g. they increase or decrease simultaneously, influencing the performance of DMFCs. The proton conductivities and methanol permeabilities for several classes of polymeric membranes are summarized in Table 1.

Perfluorosulfonic membranes, such as Nafion used as baseline in DMFCs, provide the best proton conductivity. However, membranes based on polyaromatic systems containing sulfonic groups also show conductivities comparable to Nafion, depending on their degree of sulfonation. The lowest methanol cross-over is recorded for phosphonated polyphosphazene, polysulfone and for blend or composite membranes. For the latter category, the main effect is an increase in the tortuosity factor for methanol diffusion. Sulfonated polysulfone probably provides the best compromise in terms of conductivity and cross-over; its characteristics can be further enhanced by preparing composite membranes of this polymer with inorganic fillers such as acidic silica. This comparative analysis indicates sulfonated polysulfone membranes as very

Table 1
Properties of polymer electrolyte membranes for DMFCs.

Polymer electrolyte membrane	Proton conductivity (mS cm ⁻¹)	Methanol permeability (cm ² s ⁻¹)·10 ⁶	Reference
Sulfonated poly(styrene)	50	0.52	[8]
Sulfonated poly(ether ether ketone)	70	0.3	[10]
Sulfonated poly(ether ether ketone)/zirconium oxide composite	5	0.091	[19]
Sulfonated poly(arylene ether) copolymer	100	0.81	[31]
Nafion 117	100	1.76	[41]
Co-polyimide membranes BAPS-50	40	0.33	[41]
Co-polyimide membranes BAPS-60	50	0.45	[41]
Nafion 117	75	0.9	[46]
Sulfonated polyphosphazene	35	0.13	[46]
Phosphonated polyphosphazene	55	0.14	[46]
Sulfonated poly(styrene-b-ethylene-r-butadiene-b-styrene) block copolymer	45	2.6	[62]
Nafion® 117	67	1.98	[64]
Sulfonated polysulfone	5	0.06	[80]
Nafion 115	90	1.04	[80]
Sulfonated polybenzimidazole doped	0.001	2.5	[81]
Nafion®/montmorillonite nanocomposite	78	0.1	[82]
Sulfonated polyimide	120	0.57	[9]
Nano-silica layered Nafion® composite	77	0.92	[83]
IPN of crosslinked poly(2-acrylamido-2-methyl-1-propanesulfonic acid) and Nafion®	19	1.12	[84]
IPN of Nafion® and polypyrrole	17	0.6	[85]
Sulfonated polystyrene and sulfonated poly(2,6-dimethyl-1,4-phenylene oxide) blend	34	2.35	[11]
Nafion®/poly(vinyl alcohol) blend	20	0.65	[86]
Sulfonated poly(ether ether ketone)	40	0.575	[87]
Sulfonated poly(ethersulfone)-Cardo	4	0.210	[88]
Poly(vinylidenefluoridehexafluoropropylene) copolymer/Nafion blend	2	0.2	[14]
Crosslinked poly(vinyl alcohol)/poly(2-acrylamido-2-methyl-1-propanesulfonic acid)	90	0.6	[15]
Nafion®/ORMOSILS composite	19	1.75	[89]
Sulfonated poly(styrene)/poly(tetrafluoroethylene) composite	110	0.67	[90]

promising for direct methanol fuel cell devices especially for portable applications.

3. Direct methanol fuel cell performances

3.1. Modeling and numerical simulation

The survey of the literature in the previous section has highlighted the status of worldwide research activities addressing specific polymer electrolyte materials for direct methanol fuel cells. It has been shown that the numerous physical–chemical properties of polymer membranes as well as operating conditions contribute simultaneously to determine the electrochemical fuel cell performance. Among these, fuel cell operating temperature, fuel and oxidant pressures, methanol concentration, permeability and proton conductivity of membranes should be considered. Furthermore, the DMFC performance is also influenced by the catalyst activity for the methanol oxidation (anode) and oxygen reduction (cathode) reactions, which depends on its physical–chemical characteristics (particle size, morphology) and on noble metal loading (mg cm^{-2}) in the electrodes. Experimentation is the most important tool in developing new materials and explaining the corresponding phenomena. Along with the experiments, modeling and simulation play a crucial role in providing detailed insights concerning the complex mass, heat and charged particle transport phenomena in a DMFC. A comprehensive review of the state-of-the-art modeling studies regarding mass, heat and charge transport in a DMFC is provided by H. Bahrami and A. Faghri in a recent paper [91]. They discussed the basics of kinetics and the differences between various modeling approaches and the most common terminologies in DMFC modeling. Usually, the most relevant DMFC modeling studies are divided into four topics: (i) water and methanol crossover [92,93]; (ii) coupled heat and mass transport [94–97]; (iii) enhanced system energy density [98–102]; and (iv) start-up and transient operation [103–107]. The first topic is within the scope of this review because it involves water and methanol transport through the membrane. The proposed physical models led a significant improvement in the fundamental understanding of key parameters influencing the methanol crossover through the various membranes, ranging from analytical to numerical models [108,109].

3.2. Performance analysis

The membrane properties cannot be used alone to predict DMFC performance. This because the DMFC experiments are generally not carried out by using standardized protocols, and the polymer electrolyte is not the only variable to be evaluated. Thus, it appears evident that the values of power densities are quite different also for the same type of membrane. Therefore, the literature dealing with the fuel cell performance of new polymer electrolytes is not easily comparable.

Here, we report the DMFC performance extracted and analyzed from more than 160 different papers, identified by the Scopus database. The results of this comparison are showed in Fig. 2. The performances are reported by plotting the power density of DMFCs as a function of temperature for fuel cells operating with methanol/oxygen and methanol/air feed. As already discussed, others parameters are influencing the DMFC performance such as the electrode catalyst, single cell design, reactant pressure, etc.; these should be considered but, because of their large variability, it is not easy to analyze them in detail. However, complete information and bibliographic references of different studies were reported in Table 2.

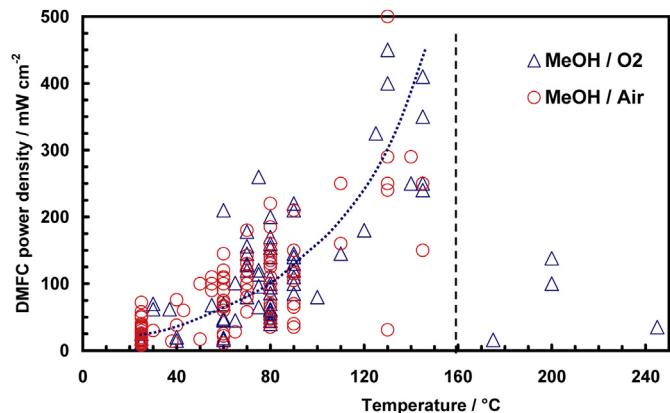


Fig. 2. DMFC power density (mW cm^{-2}) as a function of temperature ($^{\circ}\text{C}$) for different polymer electrolyte membrane-based cells operating in MeOH/oxygen (open triangle (Δ)) and in MeOH/air (open circle (\circ))).

Most of results reported in Fig. 2 are obtained from DMFCs operating at room temperature (in the figures these data have been positioned at the temperature of 25°C) and at temperatures from 60 to 90°C . A smaller number of reports concerns with temperatures within the range 25 – 60°C and above 90°C . The analysis of data shows that at low (room) and intermediate temperatures (60 – 80°C) the DMFC performances under MeOH/oxygen and MeOH/air operating conditions are similar. At temperatures from 120 to 145°C , the difference in performance becomes more marked and the power density values obtained in oxygen (open triangle) are higher, with the only exception of Ref. [53]. Above 160°C the power density values are lower than under 145°C due to the use of acid doped PBI membranes.

The similar performances at low and middle temperatures between methanol/oxygen and methanol/air are very surprising, even if there is a high scattering for the data in the literature. Obviously, power densities should be remarkably higher in methanol/oxygen because of the higher oxidant partial pressure. Moreover, the oxygen reduction reaction (ORR) in pure oxygen is also kinetically favored than in air (first order reaction). Therefore, these results put into evidence how difficult is the comparison of DMFC performances obtained from different polymer electrolytes. But, because the DMFC experiments are carried out using different procedures, in the absence of standard protocols, the results reported in Fig. 2 show significant fluctuations indicating a limited reliability. However, the analysis of experimental data of literature reported in Fig. 2 and Table 2 allows to observe that: (a) the DMFC performance for a given temperature is strongly depending on several parameters, e.g. conductivity, MeOH permeability of the membrane as well as the type of catalyst and its loading, working pressure and temperature, etc., as discussed previously. (b) DMFC performance follows an Arrhenius behavior in a wide temperature range. This means that performance is essentially related to an activated nature of processes. However, a discontinuity in this trend of power density is observed at around 160°C . This reflects a change in the electrolyte conduction mechanism from a water assisted proton transport (vehicle mechanism) to a Grotthus-type mechanism. In fact, the membranes used above 160°C are essentially based on phosphoric acid-doped polybenzimidazole. (c) The reason for the lack of a clear separation of the DMFC performance obtained with methanol/oxygen and methanol/air can be attributed mainly to uncertainty of data and/or to a marked influence of the oxygen stoichiometry, which is often not much considered in literature. Most of data collected and reported in Table 2 shows the DMFC performance obtained by using as polymer electrolyte Nafion-type membrane, Nafion-composite membrane and other electrolytes such as poly(aryl

Table 2

Summary of DMFC performance of polymer electrolyte membranes.

Polymer electrolyte membrane	1st Author/journal/year	Fuel/oxidant	Temp. (°C)	Power density (mW cm ⁻²)	Refs.
Sulfonated poly(ether ether ketone) composite silica/ZrP	Zhang, H., Solid State Ionics 2008	2 M CH ₃ OH O ₂	60	19	[110]
Sulfonated poly(ether ether ketone) blend <i>N,N</i> -bis-(1 <i>H</i> -benzimidazol-2-yl)-isophthalamide (BBImp)	Li, W., J. Power Sources 2008	2 M CH ₃ OH air	65	28	[111]
Highly fluorinated – sulfonated comb-shaped copolymer Comb 22	Kim, D.S., J. Power Sources 2008	2 M CH ₃ OH air	80	160	[112]
Sulfonated polystyrene-b-poly(dimethylsiloxane) (SPS-b-PDMS)	Lee, W., J. Membr. Sci. 2008	3 M CH ₃ OH air	25	14	[113]
Nafion/sulfated-b-cyclodextrin	Jeon, J.D., J. Power Sources 2008	2 M CH ₃ OH air	25	58	[114]
Nafion®/ZrP	Hou, H., Int. J. Hydrogen Energy 2008	5 M CH ₃ OH O ₂	75	96	[115]
Sulfonated poly(arylene ether ether nitrile) (SPAEN) copolymers	Kim, D.S., J. Membr. Sci. 2008	2 M CH ₃ OH air	80	220	[116]
Sulphonated poly(ether ether ketone) (SPEEK) and poly(benzimidazole) (PBI)	Pasupathi, S., Int. J. Hydrogen Energy 2008	1 M CH ₃ OH O ₂ active	60	45	[117]
Sulfonated poly(arylene ether benzimidazole) (SPAEBI) blend sulfonated poly(arylene ether sulfone) (SPAES)	Hong, Y.T., J. Power Sources 2008	3 M CH ₃ OH O ₂	80	110	[118]
Sulfonated poly ether ether ketone (SPEEK) hydrate oxide (SnO ₂ ·nH ₂ O)	Mecheri, B., J. Power Sources 2008	2 M CH ₃ OH O ₂	100	80	[119]
Sulfonated poly ether ether ketone (SPEEK) Functionalized ceramic powder containing surface-anchored sulfonic acid (SASA)	Lee, J.K., J. Power Sources 2008	1 M CH ₃ OH O ₂	65	45	[120]
Sulfonated polysulfone SiO ₂ composite membrane	Reichman, S., J. Power Sources 2008	1 M CH ₃ OH air	130	290	[121]
Sulfonated polysulfone	Lufrano, F., J. Power Sources 2008	2 M CH ₃ OH O ₂	120	180	[122]
Sulfonated polystyrene and fullerene composite membrane	Saga, S., J. Power Sources 2008	2 M CH ₃ OH O ₂	40	20	[122]
Nafion® and nano-size TiO ₂ –SO ₄ ²⁻ composite	Wu, Z., J. Membr. Sci. 2008	1 M CH ₃ OH air	80	47	[123]
Poly(vinyl alcohol)/hydroxyapatite (PVA/HAP)	Yang, C.C., J. Power Sources 2008	5 M CH ₃ OH O ₂	75	120	[124]
Nafion/PTFE composite membranes	Chen, L.C., J. Membr. Sci. 2008	8 M KOH + 2 M CH ₃ OH O ₂	25	12	[125]
Nafion 117	Baglio, V., J. Power Sources 2008	2 M CH ₃ OH O ₂	90	110	[126]
Sulfonated-silica/Nafion composite membrane	Yen, C.Y., J. Power Sources 2007	2 M CH ₃ OH air passive	25	20	[127]
Cross-linked fluorinated polymer alkaline membrane ADP-Morgane	Scott, K., J. Power Sources 2008	5 M CH ₃ OH O ₂	40	15	[128]
Poly(3,4-ethylenedioxy-thiophene) modified Nafion membranes	Li, L., J. Power Sources 2008	1 M CH ₃ OH O ₂	60	16	[129]
Sulfonated poly(arylene ether sulfone) – silica nanocomposite (SPAES)	Lee, C.H., J. Membr. Sci. 2007	1 M CH ₃ OH air atm	90	48	[130]
Nafion 115	Jeon, M.K., Electrochim. Acta 2007	1 M CH ₃ OH O ₂	55	68	[131]
Nafion 112	Liu, J.C., J. Power Sources 2004	4 M CH ₃ OH O ₂	25	25	[132]
Nafion 115	Liu, J., Phys. Chem. Chem. Phys. 2004	1 M CH ₃ OH O ₂	75	65	[133]
Zirconium hydrogen phosphate/disulfonated poly(arylene ether sulfone) random copolymer composite	Hill, M.L., J. Membr. Sci. 2006	0.5 M CH ₃ OH air active	80	70	[134]
Short-side-chain Hyflon® perfluorinated membranes	Antonucci, V., Desalination 2006	2 M CH ₃ OH air	140	290	[135]
Sulfonated poly(ether ether ketone) (sPEEK) 20% zirconium phosphate 12% PBI	Silva, V.S., J. Power Sources 2005	1 M CH ₃ OH air	130	31	[136]
Nafion 115	Song, S.Q., J. Power Sources 2006	1 M CH ₃ OH air	90	70	[137]
Nafion 115	Song, S.Q., J. Power Sources 2006	1 M CH ₃ OH O ₂	90	220	[138]
Disulfonated poly(arylene ether sulfone) copolymers tri-phenyl phosphine oxide (PPO)	Kim, Y.S., Polymer 2006	5 M CH ₃ OH air	80	100	[139]
Nafion 117	Cheng, X., Electrochim. Acta 2006	0.5 M CH ₃ OH air	60	25	[140]
Nafion 115	Chen, R., Electrochim. Commun. 2007	4 M CH ₃ OH O ₂ P	25	11	[141]
Nafion 115	Chen, R., J. Power Sources 2007	4 M CH ₃ OH O ₂ P	25	18	[142]
Solid acid CsH ₂ PO ₄ electrolyte.	Boysen, D.A., Science 2004	CH ₃ OH O ₂	245	35	[143]
Surface modified Nafion 115	Han, S., J. Power Sources 2007	2 M CH ₃ OH air	70	180	[144]
Blends of sulfonated poly(ether ether ketone) (sPEEK)/poly(vinylidene fluoride)	Jung, H.Y., Electrochim. Acta 2007	2 M CH ₃ OH O ₂	30	70	[145]
Nafion/poly(<i>p</i> -phenylene vinylene)	Kim, H., J. Membr. Sci. 2007	3 M CH ₃ OH air P	25	35	[146]
Organic/inorganic hybrid Nafion 115 membrane	Kim, H.K., J. Membr. Sci. 2007	3 M CH ₃ OH air P	25	15	[147]
Nafion 115	Chen, W., Electrochim. Acta 2006	1 M CH ₃ OH O ₂	90	145	[148]
Sulfonated phenol formaldehyde resin (sPFR) Nafion composite	Wu, Z., J. Power Sources 2007	5 M CH ₃ OH O ₂	75	114	[149]
Nafion	Knights, J. Power Sources 2004	0.4 M CH ₃ OH air	110	160	[150]
Nafion 117	Wang, Z.L., J. Power Sources 2006	1 M CH ₃ OH O ₂	70	178	[151]
Partially fluorinated disulfonated poly(arylene ether benzonitrile) copolymers	Sankir, M., J. Membr. Sci. 2007	0.5 M CH ₃ OH air	80	130	[152]
Nafion 115	Reshetenko, T.V., J. Power Sources 2007	3 M CH ₃ OH air P	70	90	[153]
Poly(ethylene glycol)bis(carboxymethyl)ether plasticized PVA/PAMPS proton-conducting semi-IPNs	Qiao, J. Electrochim. Commun. 2007	10% CH ₃ OH O ₂ active	80	50	[154]

Table 2 (continued)

Polymer electrolyte membrane	1st Author/journal/year	Fuel/oxidant	Temp. (°C)	Power density (mW cm ⁻²)	Refs.
Nafion® ionomer with functionalized montmorillonite (MMT)	Lee, W., J. Membr. Sci. 2007	3 M CH ₃ OH air P	25	72	[154]
Cross-linked poly(vinyl alcohol) and poly(styrene sulfonic acid-co-maleic anhydride)-based semi-interpenetrating network	Lin, C.W., J. Power Sources 2007	2 M CH ₃ OH O ₂	80	100	[155]
Nafion 117	Martin, J.J., J. Power Sources 2007	2 M CH ₃ OH air P	25	8	[156]
Nafion 115	Liu, Y., J. Power Sources 2007	1 M CH ₃ OH air	55	90	[157]
Nafion 115	Liu, J., J. Power Sources 2004	1 M CH ₃ OH air P	25	26	[133]
Sulfonated poly(propylene oxide) oligomers/Nafion acid–base blend membranes	Lin, Y.F., J. Power Sources 2007	2 M CH ₃ OH air	60	72	[158]
Nafion and silica composite membrane	Antonucci, P.L., Solid State Ionics 1999	2 M CH ₃ OH O ₂	145	250	[159]
Nafion and silica composite membrane	Antonucci, P.L., Solid State Ionics 1999	2 M CH ₃ OH air	145	150	[159]
Nafion and silica composite membrane	Arico, A.S., J. Power Sources 2000	2 M CH ₃ OH O ₂ SFF	130	450	[160]
Nafion and silica composite membrane	Arico, A.S., J. Power Sources 2000	2 M CH ₃ OH air SFF	130	290	[160]
Nafion and titanium oxide composite membrane	Baglio, V., Electrochim. Acta 2005	2 M CH ₃ OH O ₂	145	350	[161]
Nafion 117	Baldauf, M., J. Power Sources 1999	2 M CH ₃ OH O ₂	140	250	[162]
Nafion 117	Baldauf, M., J. Power Sources 1999	0.5 M CH ₃ OH air	80	90	[162]
Nano nonporous (PVDF) proton-conducting membrane (PCM)	Blum, A., J. Power Sources 2003	1 M CH ₃ OH air	25	12	[163]
Nafion 117	Chen, C.Y., J. Power Sources 2003	3% CH ₃ OH air P	25	20	[164]
Nafion 117	Dohle, H., J. Power Sources 2002	1 M CH ₃ OH air stack	80	100	[165]
Sulfonated naphthalene dianhydride based polyimide copolymers	Einsla, B.R., J. Membr. Sci. 2005	2 M CH ₃ OH air	80	150	[41]
Nafion115/silicon oxide composite membranes	Jung, D.H., J. Power Sources 2002	2 M CH ₃ OH O ₂	125	325	[166]
Nafion 115	Kim, J.D., J. Power Sources 2004	4 M CH ₃ OH air P	25	40	[167]
Sulfonated poly(ether ether ketone) (SPEEK) membranes	Li, L., J. Membr. Sci. 2003	2 M CH ₃ OH O ₂	80	60	[19]
Nafion 112 membrane	Lim, C., J. Power Sources 2003	2 M CH ₃ OH air	90	210	[168]
Nafion 112 membrane	Qi, Z., J. Power Sources 2002	1 M CH ₃ OH air	80	35	[169]
Radiation-grafted membranes based on polyethylene and ETFE	Scott, K., J. Membr. Sci. 2000	2 M CH ₃ OH air	90	65	[57]
Nafion polyvinyl alcohol composite membrane	Shao, Z.G., J. Membr. Sci. 2002	2 M CH ₃ OH O ₂	90	100	[170]
Nafion 112 membrane	Shukla, A.K., J. Power Sources 1998	2 M CH ₃ OH air	90	40	[171]
Nafion 115	Song, S., Appl. Catal. B 2006	1 M CH ₃ OH O ₂	90	140	[172]
Nafion-silica-phosphotungstic acid composite membrane	Staiti, P., Solid State Ionics 2001	2 M CH ₃ OH air	145	250	[173]
Nafion 115 membrane	Wei, Z., J. Power Sources 2002	1 M CH ₃ OH air	90	115	[174]
Polypropylene (PP)-g-sulfonated polystyrene (SPS) composite membranes	Bae, B., J. Membr. Sci. 2003	3 M CH ₃ OH air	25	16	[12]
Nafion 117 membrane	Elabd, Y.A., J. Membr. Sci. 2004	1 M CH ₃ OH air	80	110	[175]
Nafion 117 membrane	Ge, J., J. Power Sources 2005	2 M CH ₃ OH air	70	80	[176]
Thin layer polybenzimidazole on Nafion 117 membrane	Hobson, L.J., J. Power Sources 2002	2 M CH ₃ OH air	60	22	[177]
Composite recast silica/Nafion membranes	Jiang, R., J. Membr. Sci. 2006	1 M CH ₃ OH air	60	65	[178]
Nafion 117 membrane	Lizcano-Valbuena, WH, Electrochim. Acta 2003	2 M CH ₃ OH O ₂	90	85	[179]
Nafion 112 membrane	Lu, Q.C., J. Power Sources 2005	2 M CH ₃ OH air	60	100	[180]
Nafion 112 membrane	Nakagawa, N., J. Power Sources 2003	2 M CH ₃ OH air	90	70	[181]
Nafion 117 membrane	Rousseau, S., J. Power Sources 2006	2 M C ₂ H ₅ OH O ₂	80	50	[182]
Multilayer Nafion – poly(ether ether ketone) – Nafion membranes	Yang, B., Electrochim. Commun. 2004	2 M CH ₃ OH O ₂	80	40	[183]
Nafion-silica-phosphotungstic acid composite membrane	Aricò, A.S., Electrochim. Commun. 2003	2 M CH ₃ OH O ₂	145	410	[184]
Cross-linked fluorinated polymer; Morgane®-ADP membrane	Yu, E.H., J. Power Sources 2004	2 M CH ₃ OH/1 M NaOH air	60	11	[185]
Grafted membrane based on poly(ethylene-tetrafluoro ethylene), or ETFE, film.	Hatanaka, T., Fuel 2002	1 M CH ₃ OH air	80	65	[58]
Blend of sulfonated polystyrene (sPS) and partially sulfonated poly(2,6-dimethyl-1,4-phenylene oxide) (sPPO)	Jung, B., J. Membr. Sci. 2004	2 M CH ₃ OH air	50	17	[11]
Sulfonated styrene-(ethylene-butylene)-sulfonated styrene (SEBSS) copolymer	Jung, D.H., Int. J. Hydrogen Energy 2001	2 M CH ₃ OH O ₂	90	120	[13]
Ionomically cross-linked polyaryl sulfonate and a poly-aryl N base polymers	Kerres, J., Desalination 2002	1 M CH ₃ OH air	110	250	[186]
Nafion 115 membrane	Kho, B.K., Electrochim. Acta 2004	3 M CH ₃ OH air passive	25	52	[187]
Nafion 117	Kim, J.-H., J. Power Sources 2004	2 M CH ₃ OH O ₂	80	170	[188]
Nafion 117	Lindermeir, A., J. Power Sources 2004	0.75 M CH ₃ OH O ₂	80	160	[189]

(continued on next page)

Table 2 (continued)

Polymer electrolyte membrane	1st Author/journal/year	Fuel/oxidant	Temp. (°C)	Power density (mW cm ⁻²)	Refs.
Nafion 115	Li, W., J. Phys. Chem. B 2006	1 M CH ₃ OH O ₂	90	130	[190]
Nafion 117	Neergat, M., J. Power Sources 2002	2 M CH ₃ OH air	90	105	[191]
Grafted polyvinylidene fluoride (PVDF) membranes	Shen, M., J. Membr. Sci. 2005	2 M CH ₃ OH air	80	35	[192]
Nafion 115 membrane	Yang, H., Electrochim. Acta 2005	1 M CH ₃ OH O ₂	60	70	[193]
Nafion silica phosphotungstic acid (PWA) composite membranes	Xu, W., Electrochim. Acta 2005	2 M CH ₃ OH O ₂	80	70	[194]
Nafion 112 membrane	Xie, C., J. Power Sources 2004	1 M CH ₃ OH air stack	43	60	[195]
Nafion 115 membrane	Wang, S., Electrochim. Commun. 2005	1 M CH ₃ OH O ₂	75	260	[196]
Nafion 112 membrane	Ren, X., J. Electrochem. Soc. 1996	1 M CH ₃ OH O ₂	130	400	[197]
Nafion 112 membrane	Ren, X., J. Electrochem. Soc. 1996	1 M CH ₃ OH air	130	250	[197]
Disulfonated poly(arylene ether benzonitrile) copolymers	Kim, Y.S., J. Electrochem. Soc. 2004	5 M CH ₃ OH air	80	100	[31]
Nafion/acid functionalized zeolite Beta membrane	Chen, Z., Chem. Mater. 2006	5 M CH ₃ OH O ₂	70	120	[198]
Sulfonated poly(ether ether ketone) sPEEK membranes	Jung, H.Y., J. Power Sources 2006	2 M CH ₃ OH O ₂	30	62	[199]
Sulfonated polysulfone	Fu, Y.Z., J. Power Sources 2006	2 M CH ₃ OH O ₂	80	62	[200]
Nafion 115 membrane	Wang, G., Electrochim. Solid State Lett. 2005	1 M CH ₃ OH air	90	150	[201]
Ionically cross-linked SPEEK-PBI membranes	Kerres, J., Fuel cells 2004	1 M CH ₃ OH air	130	240	[202]
Disulfonated poly(arylene ether sulfones) random copolymers	Harrison, W.L., Fuel cells 2005	0.5 M CH ₃ OH air	80	125	[30]
Acid doped polybenzimidazole	Wang, J.-T., J. Appl. Electrochem. 1996	2 M CH ₃ OH O ₂	200	100	[203]
Acid doped polybenzimidazole Caltec V – PBI – BASF	Gubler, L., J. Electrochem. Soc. 2007	1 M CH ₃ OH O ₂	110	145	[204]
Acid doped polybenzimidazole	Lobato, J., Energy Fuels 2008	~10 M (V) CH ₃ OH O ₂	200	138	[205]
Nano nonporous (PVDF) proton-conducting membrane (PCM) + 1.7 M triflic acid	Peled, E., Electrochim. Solid State Lett. 2004	1 M CH ₃ OH + 1.7 triflic acid/air	130	500	[54]
Nafion silica composite membrane	Arico, A.S., Electrochim. Solid State Lett. 1998	2 M CH ₃ OH O ₂	145	240	[69]
Sulfonated polysulfone	Lufrano, F., J. Power sources 2010	1 M CH ₃ OH air	25	38	[206]
Nafion 117	Ahmad, M.M., Energy Convers. Manage. 2010	4 M CH ₃ OH air passive	25	14	[207]
Nafion 1135	Cao, J., Int. J. Hydrogen Energy 2010	3 M CH ₃ OH air passive	25	33	[208]
Sulfonated polyimide (SPI)	Chen, K., J. Membr. Sci. 2010	1 M CH ₃ OH air passive	60	90	[209]
Sulfonated polyetheretherketone mesoporous benzene-silica composite membranes	Chen, K., J. Membr. Sci. 2010	2 M CH ₃ OH O ₂	80	56	[209]
Nafion/PI–PVA–TSPS composite membranes	Fang, Y., Electrochim. Acta 2010	1.5 M CH ₃ OH air	55	100	[210]
Poly(styrene sulfonic acid)-grafted PVDF-HFP/tin oxide composite	G. Gnana Kumar, J. Membr. Sci. 2010	2 M CH ₃ OH air	60	110	[211]
SEEK/SDPS-DP-60/sPEEK multilayer membrane	Li, W., J. Power Sources 2010	1 M CH ₃ OH O ₂	80	140	[212]
Ph-SPEEK + 5 wt% 5-amino-benzotriazole (PSf-BTraz)	Li, W., Electrochim. Commun. 2010	5 M CH ₃ OH O ₂	80	154	[213]
Sulphonated biphenylated poly(ether ether ketone) (BiPh-SPEEKDK)	Liu, B., Fuel Cells 2010	2 M CH ₃ OH air	80	140	[214]
Polyimide/Nafion composite membrane	Nguyen, T., J. Power Sources 2010	5 M CH ₃ OH O ₂	70	128	[215]
Nafion 115	Y.-C. Park, Int. J. Hydrogen Energy 2010	2 M CH ₃ OH air	60	108	[216]
Poly(vinyl alcohol)/3-trimethylammonium propyl funct. silica (PVA-TMAPS)	E.D. Wang, Int. J. Hydrogen Energy 2010	3 M C ₂ H ₅ OH 5 M KOH O ₂	60	46	[217]
Poly(vinyl alcohol)/TiO ₂ nanotubes/poly(styrene sulfonic acid) (PVA/nt-TiO ₂ /PSSA) composite membrane	C.-C. Yang, J. Power Sources 2010	2 M CH ₃ OH air active	25	24	[218]
Quaternized poly(vinyl alcohol)/alumina – QPVA/Al2O3	C.-C. Yang, J. Power Sources 2010	4 M CH ₃ OH/4 M KOH air	25	36	[219]
Nafion 115	C. Xu, Int. J. Hydrogen Energy 2010	3 M CH ₃ OH air passive	25	50	[220]
Nafion/ZrP composite	C. Arbizzani, J. Power Sources 2010	1 M CH ₃ OH O ₂	80	44	[221]
Nafion 117	L. Feng, J. Power Sources 2011	3 M CH ₃ OH air passive	25	21	[222]
Sulfonated poly(ether sulfone) organically treated montmorillonite (OMMT) composite membrane	Hasani-Sadrabadi, M. M., Renewable Energy 2010	4 M CH ₃ OH O ₂	70	130	[223]
Nafion 112	Tsujiguchi, T., J. Power Sources 2010	100% CH ₃ OH air passive	25	30	[224]
SPEEK/PSf-BTraz	Li, W., J. Membr. Sci. 2010	1 M CH ₃ OH O ₂	65	101	[225]
Poly(vinylalcohol)/montmorillonite/poly(styrene sulfonic acid) (PVA/MMT/PSSA) composite membrane	Yang, C.C., Int. J. Hydrogen Energy 2011	2 M CH ₃ OH air breath.	25	20	[226]
Polyethylene vinyl ether styrene sulfonic acid membrane	V. Baglio et al./Electrochim. Acta 2010	2 M CH ₃ OH air breath. mini-stack	25	18	[227]
Cross-linked norbornene sulfonated poly(ether ketone)s – NB-sPEEK-80×	L.-K. Chen, J. Membr. Sci. 2010	1 M CH ₃ OH O ₂	60	16.5	[228]
Nafion 117	Y.-J. Chiu, J. Power Sources 2011	1.5 M CH ₃ OH air	60	100	[229]

Table 2 (continued)

Polymer electrolyte membrane	1st Author/journal/year	Fuel/oxidant	Temp. (°C)	Power density (mW cm ⁻²)	Refs.
Nafion/PI-PVA-TSPS composite membranes	Y. Fang, Electrochim. Acta 2010	1.5 M CH ₃ OH air	55	100	[210]
Nafion 115	N. Jung, Electrochim. Commun. 2010	1 M CH ₃ OH air	70	120	[230]
Poly (2,6-dimethyl-1,4-phenylene oxide) (SPPO)-polybenzimidazole (PBI) blend membranes	A.H. Haghghi, Int. J. Hydrogen Energy 2011	5 M CH ₃ OH air	70	58	[231]
Multi-layer chitosan biopolymer on Nafion 105 membranes	M.M. Hasani-Sadrabadi, Polymer 2012	1 M CH ₃ OH air	70	100	[232]
Semi-interpenetrating polymer network (semi-IPN) organosiloxane-based organic/inorganic hybrid	D.X. Luu, J. Power Sources 2011	1 M CH ₃ OH air	80	135	[233]
Sulfophenylated poly(arylene ether ketone) membrane – Ph-m-SPEEK	B. Liu, Electrochim. Acta 2010	1 M CH ₃ OH air	80	185	[234]
Multilayered sulphonated polysulfone/silica composite membranes	R. Padmavathi, Electrochim. Acta 2012	1 M CH ₃ OH O ₂	80	86	[235]
Nafion 115	Y.C. Park, J. Power Sources 2010	1 M CH ₃ OH air P stack	50	100	[236]
Sulphonated poly(ether ether ketone)s (MS-SPEEKs)	J.C. Tsai, J. Power Sources 2011	2 M CH ₃ OH O ₂	80	95	[237]
Nafion 115	T. Ward, Int. J. Hydrogen Energy 2011	1 M CH ₃ OH air passive tubular	40	38	[238]
Sulfonated poly(ether ether ketone) sulfonated cyclodextrin membranes	T. Yang, Int. J. Hydrogen Energy 2011	8 M CH ₃ OH air passive	30	30	[239]
Sulfonated polybenzimidazole/phosphoric acid doped	M. Mamlouk, J. Fuel Cell Sci. Technol. 2011	2 M CH ₃ OH O ₂	175	16	[240]
Sulfonated poly(arylene ether sulfone) random copolymers SPAES-BP(90)/SPAES-HPF(10)	S.Y. Oh, Macromol. Res. 2012	2 M CH ₃ OH air	60	145	[241]
Sulfonated poly(phenylene oxide)/sulfonated poly(ether ether ketone) (S-PPO/S-PEEK MMT hybrid	M.M. Hasani-Sadrabadi, Solid State Ionics 2009	5 M CH ₃ OH O ₂	70	145	[242]
Sulfonated poly(ether sulfone)/sulfonated polybenzimidazole blend membranes	N.N. Krishnan, Eur. Polym. J. 2010	2 M CH ₃ OH air	70	110	[243]
Sulfonated polysulfone and acidic silica composite (SPSF-SiO ₂ -OSO ₃ H)	F. Lufrano, Phys. Chem. Chem. Phys. 2012	1 M CH ₃ OH air	60	60	[244]
Sulfonated poly(arylene ether sulfone)-clay sPAS-C composites	Y.S. Choi, Adv. Mater. 2008	1 M CH ₃ OH air	70	142	[245]
Nafion-PBI-ZP hybrid membrane	H. Ahmad, Int. J. Hydrogen Energy 2011	5 M CH ₃ OH air passive	25	10	[246]
Nafion 117	L. Feng, Fuel 2012	4 M CH ₃ OH air passive	25	26	[247]
Nafion 117	V.B. Silva, Appl. Math. Comput. 2012	1.4 M CH ₃ OH air passive	90	70	[248]
Hydrocarbon membrane	J.Y. Park, Int. J. Hydrogen Energy 2012	1 M CH ₃ OH air stack	60	67	[249]
Chitosan (CS)-polyvinyl alcohol (PVA)/sulfosuccinic acid SSA)/glutaraldehyde (GA) – (SWA)	S. Meenakshi, J. Solid State Electrochem. 2012	2 M CH ₃ OH O ₂	70	156	[250]
Sulfonated poly(imide) SPI-50	J. Yan, Int. J. Hydrogen Energy 2012	2 M CH ₃ OH air	60	75	[251]
Sulfonated poly ether ether ketone (SPEEK) SiO ₂ PWA composite membranes	G. Zhang, J. Wuhan Univ. Technol., 2011	2 M CH ₃ OH O ₂	80	45	[252]
Nafion 117	A.D. Moore, RSC Adv. 2012	1 M CH ₃ OH air	90	35	[253]
PVdf-HFP silica sulfuric acid composite membranes	G. Gnana Kumar, Curr. Appl. Phys. 2011	2 M CH ₃ OH air	80	43	[254]
Nafion – purple membrane (PM) composite membranes	J. Zhang, J. Membr. Sci. 2011	1.5 M CH ₃ OH O ₂	37	62	[255]
Nafion 115	K. Nam, Int. J. Hydrogen Energy 2012	2 M CH ₃ OH air	60	120	[256]
Nafion 117	X. Xue, Fuel Cells 2011	2 M CH ₃ OH air	60	100	[257]
Sulfophenylated poly(ether ether ketone) (Ph-SPEEK) acid-base blend	W. Li, Electrochim. Commun. 2010	5 M CH ₃ OH air	80	160	[213]
Nafion 117	T. Hyeon, Angew. Chem. Int. Ed. 2003	2 M CH ₃ OH O ₂	60	210	[258]
Nafion 115	J. Qi, Carbon 2012	1 M CH ₃ OH O ₂	90	210	[259]
Poly(arylene ether sulfone)s containing pendant sulfonic acid groups	J.K. Lee, J. Membr. Sci. 2009	1 M CH ₃ OH O ₂	80	100	[260]
Hydrocarbon membrane 25 μm (Tokuyama, C255) JP	M. Kosaka, J. Phys. Chem. C 2009	2 M CH ₃ OH air passive	40	76	[261]
Sulfonated poly(phthalazinone ether ketone) (SPPEK) impregnated microporous Film (SPPEK-PE)	M.H. Yildirim, J. Membr. Sci. 2009	6 M CH ₃ OH O ₂	80	200	[262]

ether sulfone)s, polysulfones and poly(ether sulfone)s. A smaller amount of studies deals with MEAs equipped with poly(ether ketone)s and with other types of hydrocarbon membranes.

Fig. 3 shows in an Arrhenius plot the power density as a function of the temperature for polymer electrolyte membranes in DMFCs using oxygen as oxidant. A large scattering in the data is observed.

The trend of the Arrhenius behavior with the temperature is clear, but the data scatter ($R^2 = 0.25$) is indicating that the results are highly influenced from the polymer electrolyte and how measurements are performed. A large number of data concerns with the range of temperatures between 70 and 90 °C, which is the typical application of polymer electrolyte fuel cells. The scattering

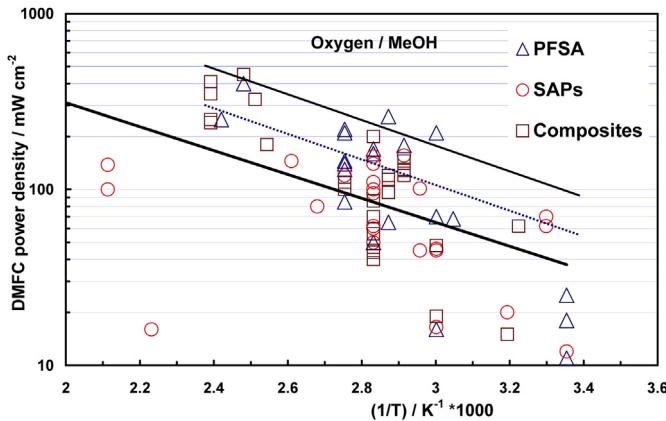


Fig. 3. The Arrhenius plot of power density (mW cm^{-2}) for DMFCs equipped with different polymer membranes operating in MeOH/oxygen.

of data is high; for example, at 80 °C the reported power densities vary from about 40 to 200 mW cm^{-2} , which is not explained if we consider just the differences in proton conductivity. Furthermore, also for some Nafion membrane-based cells there is this large variation of performance. This scattering could also be due to the variability of the procedure used to collect the data in the different laboratories. Another variable concerns with the methanol crossover that is also related to the operating conditions. The highest value of DMFC performance of 200 mW cm^{-2} at 80 °C was reported by Yildirim et al. [262] for a SPPEK–PE composite membrane in 6 M MeOH/O₂. At 60 °C the DMFC performance varies between 15 and 210 mW cm^{-2} . At 70 °C a peak of 178 mW cm^{-2} was reported by Wang et al. [151] for a Nafion 117 membrane in 1 M MeOH/O₂ and with a catalyst loading of 1.5 mg cm^{-2} (the catalyst was an 80 wt% Pt–Ru/C) at the anode and 1.2 mg cm^{-2} (40 wt% Pt/C) at the cathode. Another power peak of 260 mW cm^{-2} [196] was reported for a Nafion 115 membrane in 1 M MeOH/O₂ at 75 °C and with a catalyst loading of 3.7 mg cm^{-2} of Pt–Ru black at the anode and 2.3 mg cm^{-2} of Pt black at the cathode. At temperatures from 120 to 145 °C, the DMFC performance reached values as high as 400 mW cm^{-2} because both oxygen reduction reaction (ORR) and methanol electro-oxidation kinetics are favored. This level of performance has been reported for DMFCs equipped with Nafion/silica composite [160,184], Nafion/titania composite [161] and Nafion 112 membranes [197]. These results demonstrated the positive influence of filler acidity on the water retention properties of the membrane and, thus, a better conductivity and performance at higher temperatures [6]. Accordingly, another composite membrane based on sulfonated polysulfone reached a remarkable maximum power density of 180 mW cm^{-2} at $T = 120$ °C [122].

A mathematical fitting of data with an exponential function has been used to find a trend of DMFC performance with the temperature. This is reported in Fig. 3. However, a correlation factor of $R^2 = 0.25$ indicates poor correlation of data.

The upper limit of power densities is about 200 and 350–400 mW cm^{-2} for temperatures of 80° and 145 °C, respectively, in the presence of O₂ feed. A relevant performance of 400 mW cm^{-2} is reported in some papers [160,161,184,197]. This is not significantly different from H₂-air fuel cells. The non-linear fitting-curve in Figs. 3 and 4 is a visual guideline and is an indication of a mean DMFC performance for a specific temperature and for a whole set of experimental data. From an in-depth analysis of the data, it can be considered that the results above the fitting-curve could be even more accurate than those under the curve. In fact, the latter appear to suffer of poor accuracy. Because of this high variability of data regarding DMFC performance there is no realistic indication about

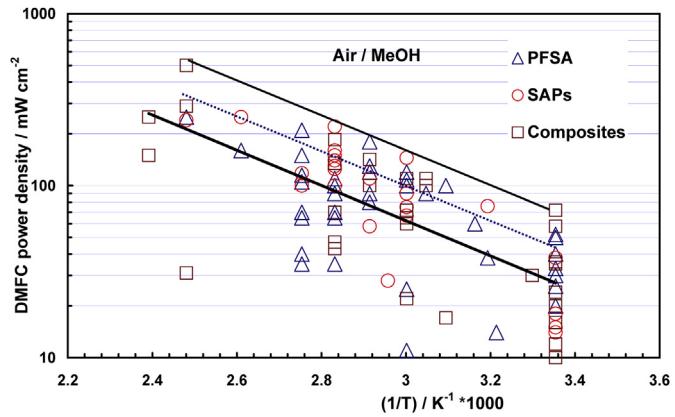


Fig. 4. The Arrhenius plot of power density (mW cm^{-2}) for DMFCs equipped with different polymer membranes operating in MeOH/air.

power density that can be achieved with polymer electrolytes alternative to Nafion. To establish a method for comparing the data obtained with different polymer electrolytes, we have drawn an arbitrary curve that we define as an upper bound relationship shifted up with respect to the exponential curve fitting. This area between the two lines (average values and upper bound) can be used as a confidentiality region where the DMFC performance of new polymer electrolytes should fall if accurate measurements are carried out. Thus, this region, in the absence of a standard method of DMFC measurements, could be used to assess the goodness and accuracy of new results of literature. In practice, if new results, obtained with a good reproducibility and accuracy of measurements, are positioned in the upper part of the graph they could indicate excellent performance. Upon progressing in this field, this upper bound relationship could be revised and used to accredit new research trends for new polymer electrolytes proposed for DMFC applications.

Fig. 4 shows the results of power density in methanol/air DMFCs for the different polymer electrolytes as a function of temperature. The data of this figure have been obtained from more than one hundreds of papers and also here a large scattering of data at all temperatures was observed. It is likely that these differences in DMFC performance are not only due to the reasons above discussed but also to the accuracy and reproducibility of experimental results. Many of these results could be underestimated because obtained in research labs with low experience in fuel cell measurements. Hence, it is expected that some of these performances could be lower than the realistic one obtainable from appropriate measurements. Thus, because of these drawbacks also the fitting-curve could be underestimated with respect to real values, and it is likely that points above the fitting could be those with major credential, taking into account the large difference in DMFC performances, e.g. at room temperature the power density values range from 10 to 72 mW cm^{-2} . Also at 80 °C, the differences are relevant (the maximum value is 6.3 times higher than minimum). These observations clearly demonstrate that the differences cannot be only explained on the basis of polymer electrolyte properties such as proton conductivity, methanol permeability, etc. but they are rather due to the reasons previously discussed. A specific difference between the data of Fig. 3 (oxygen feed) with those of Fig. 4 (air feed) concerns the fact that the power density in the latter figure varies at a lower rate with the increase of temperature. The majority of DMFC performances is obtained with methanol/air fuel cells operating at room temperature in single cells and small size stacks. Generally, small single cells and stacks were tested under air breathing (passive mode) because these conditions are of interest in portable applications.

The highest performance at room temperature was reported for a cell based on organic/inorganic composite-Nafion membrane in air-breathing mode [154], in which the catalyst loading of unsupported PtRu and Pt was 8 mg cm⁻² at both anode and cathode, and the active geometric area of electrodes was 10 cm². At temperatures of 60–80 °C the DMFC performance varied from 180 to 220 mW cm⁻². A peak value of 220 mW cm⁻² at 80 °C was reported by Kim et al. [116] for a sulfonated poly(arylene ether ether nitrile) (SPEAEN) copolymer in 1 M MeOH/air, with a catalyst loading of 10 mg cm⁻² for the unsupported Pt–Ru and of 6 mg cm⁻² for Pt at the anode and cathode, respectively. At the temperature of 110 °C, a high performance was obtained for blend membranes based on ionically cross-linked polyaryl sulfonated and poly-aryl-N bases [186] in 1 M MeOH/air and with a catalyst loading of 6.4 mg cm⁻² for Pt–Ru black at anode and 5.3 mg cm⁻² for Pt black at cathode. For temperatures ranging from 130 to 145 °C, the DMFC performance reached values as high as 250–290 mW cm⁻² [186].

In general, although proton conductivity, methanol cross-over and selectivities, e.g. the ratio between conductivity and methanol cross-over, are practical parameters to make useful comparisons among different polymer electrolytes, they cannot be used with confidence to predict DMFC performances. Thus, as it may be expected, there is the necessity to validate the fuel cell performance for new polymer electrolytes under rigorous conditions that should be obtained from standardized methods. The validation of DMFC performance for new polymer electrolytes should be certified from accredited laboratories following specific standard protocols. This review could represent a useful tool for comparing the new results obtained in the field of DMFCs.

4. Conclusion

Advances in research and development (R&D) of polymer electrolyte membranes for direct methanol fuel cell applications have been reviewed. Several classes of polymer membranes were analyzed in terms of structure, physical, chemical and electrochemical properties. The properties of different polymer electrolytes were analyzed on the basis of methanol permeability, proton conductivity and DMFC performance. The analysis of DMFC performance values reported in more than 160 papers does not allow an easy comparison among the different membranes and nor indicates which are the best polymer electrolytes for DMFC application at specific temperatures. Most of the papers reporting high DMFC performance are dealing with perfluorosulfonate polymer (Nafion type) electrolytes. This is likely due to a higher knowledge of Nafion properties compared to alternative membranes. Aromatic polymers seem to be potentially suitable for DMFC applications and competing with Nafion membranes in terms of fuel cells performance. At temperatures above 100 °C, composite membranes based on perfluorinated and aromatic polymer electrolytes show clear advantages compared to bare sulfonated polymers because of the higher proton conductivity at $T > 100$ °C resulting from improved water retention properties. An analysis of literature also shows that methanol permeability and proton conductivity are significant properties but cannot be used with confidence to predict the potential use of novel polymers in DMFC applications. Moreover, this study shows that DMFC performance in methanol/air is similar to that of methanol/oxygen in the low temperature range. This finding is unexpected because the oxygen reaction reduction is favored in the presence of pure oxygen rather than air. This may be due to several aspects, including the general use of large oxygen stoichiometry at the cathode in the presence of air. Of course, this may cause a significant loss of energy on the air blower at the system level. These aspects are often not reported, making a critical analysis of the performance quite difficult.

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